Removal of Pb, Zn and Cu ions by zeolite/soil models treated with urban wastewater.

Vacca, S.[1*] – Capra, G. F.[1] – Duras, M. G.[1] – Selis, G.[1] – Buondonno, A.[2] – Cabula, E.[1]

[1]Dipartimento di Botanica ed Ecologia Vegetale, Università di Sassari, Sa Terra Mala, 08100 Nuoro, Italy, *Tel: +39 0784/214948; Fax: +39 0784/205292; E-mail: pedolnu@uniss.it
[2]Dipartimento di Scienze Ambientali, II Università di Napoli (Caserta), Italy

1. Abstract

This research focused on the removal performance of Pb, Zn and Cu ions by the use of zeolite/soil models treated with urban wastewater. Two different types of zeolite (clinoptilolite and yellow Neapolitan tuff) and soil (sandy soil and clay soil) in different percentages (0%, 25%, 50%, 100%) were used. The models were treated with two different kinds of urban wastewater: urban wastewater following sewage treatment system and urban wastewater artificially polluted with standard reagent.

The study shows that the removal capacity of Pb, Zn and Cu ions by zeolite/soil models is not only due to the kind of zeolite but also to its percentage in the model.

2. Introduction

In the last twenty years quantity and quality of available water resources was sensitively reduced by the recurrent droughts (ESA, 2001; Jackson R.B. et al., 2001); moreover, there has been an increasing demand from all the productive sectors (Postel S.L. et al., 1996). As a consequence of such requests, strong reductions of water availabilities are recorded (ESA, 2001; Postel S.L. et al., 1996; Vorosmarty C.J. et al., 2000) and a remedy, even though partial, can be represented by the practice of wastewaters reuse in agriculture that allows to make the so-called "not conventional" resources available, so that the employ of more valuable supplying sources can be limited (Van der Hoek W. et al., 2002; Asano T., Raise A.D of it., 1996; Blumethal U.J. et al., 2000).

Besides, employment of treated wastewaters for irrigation represents the possibility of a profitable use for those waters whose disposal results problematic, and also the possibility of recovering the nutrients dissolved in them (Nuvoli S., Matina P., 2002). In this research, the analyses conducted on the principal alkaline and alkaline-earth elements and on some heavy metals have shown that these elements, in low concentrations, result fundamental to stimulate vegetable growth, biological activity, and to increase the possible productive yield in environmental sectors with economic finality (agriculture, horticulture, etc.). Besides, the investigated samples show notable advantages such as: non-toxicity and natural origin of materials; their easy application in various sectors and by different operators; the ecological advantage determined by the ability to gradually release nutrients. Considering what has been said before, wastewaters reuse hypotheses have some effects that, even if interesting principally in the agriculture sector, also involve other divisions as the environment and the tourism, with consequent socio-economic benefits.

The use evaluation of natural zeolitizated material, as tuffs, as soil conditioners for impacts mitigation is of remarkable interest. Particularly, the zeolitic phases observed in such rocks could develop a decisive role in the relationships water / ground rebalance, in the toxic elements adsorption and in the nutrient availability regulation (Hui K.S. et al., 2005). In fact natural zeolite are characterized by elevated ion exchange capacity, high porosity and hydraulic capacity, high surface reactivity and catalytic activity (Rehàkovà M. et al., 2004).

3. Methods

With the aim to identify environmental restoration strategies of low cost and low environmental impact, also according with the legislation in force, as well as extending the possibilities of using natural zeolite in Applied Pedology and Pedotechnique sectors [Van Ouwerkerk and Koolen, 1988], appropriate models have been realized, in confined environment, with the aim to isolate and to individualize the effects due to the discrete components of the model. Two different types of zeolite (clinoptilolite and yellow Neapolitan tuff) and soil (sandy soil and clay soil) in different percentages (0%, 25%, 50%, 100%) were used. The zeolites selected for the realization of this research project are the Clinoptilolite and the Yellow Neapolitan Tuff.

The two different zeolite typologies have been added to two soil typologies (an alkaline sandy soil of the coastal dune of Castel Volturno pine forest and an acid clay soil of Ottana), and subsequently submitted to treatment with urban wastewater coming from the new municipal wastewater power plant of Nuoro.

The research protocol had two phases, in the first one the purpose was to try to evaluate the possibility of soil / zeolite mixtures utilization to mitigate the impact of a real wastewater as that of the municipal wastewater power plant of Nuoro. The second phase of the study, instead, following the same scheme adopted in the first phase of the research, was focused on the assessment of the effect of these mixtures on an artificial wastewater, representative of extreme conditions of pollution (the wastewater used in the first phase of the experimentation was in fact conforming to the limits of law, therefore poorly contaminated).

The wastewaters analyses as well as those on the outflowing percolate have been conducted according with the Analytical Official Methods for the Waters of the APAT and the IRSA-CNR. For the soil analyses the reference were the Soil Chemical Analysis Methods of the Agricultural and Forest Politics Ministry.

4. Results

The obtained results are represented in schematic way in the Chart 1. The experimental tests, conducted in confined environment, have shown the followings aspects:

- at the end of the contact tests with the purified wastewater it is possible to notice that, in all the investigated samples, lead, copper and zinc concentrations (in reference to the only parameters submitted to law limits) don't overcome in any case limits settled by the legislation in force. Under these conditions of extremely limited concentrations of metals in the wastewater, the adopted samples primarily tend to introduce, rather than to subtract, lead, zinc and copper. The only exception is represented by the removal of copper in the samples with a mineral matrix only (zeolite);
- at the end of contact tests with the artificial wastewater, despite the conditions of extreme pollution imposed on the wastewater, all the three metals result abundantly below the limits defined by the normative in force;
- the chemical-physical characteristics of the wastewater result significant in the removal efficiencies of the samples ground / zeolite, with often different trends for same samples but treated with different typologies of wastewater;
- the chemical-physical and mineralogical characteristics of the two zeolite typologies used in the contact tests can determine different trends in the investigated samples. Several studies emphasize the different removal abilities and selectivity of the different zeolite typologies towards the heavy metals (Blanchard G. et al., 1984; Inglezakis V.J. et al., 2003; Lin C.F., Hsi H.C., 1995; Querol X. et al., 2002). In many of these studies, the authors consider the adsorption capacities of different zeolite typologies in regards to one element only, therefore it is difficult to apply the same conclusions when capacities must be assessed considering more elements (Hui K.S. et al., 2005). However in the international bibliography it is possible to find references related to the adsorption capacities shown by different zeolite typologies submitted to treatment with different heavy metals. Also in these studies, as we observed, the initial concentration of the pollutant plays a critical role in the pollutant blasting performances in solution (Ouki S.K., Kavannagh M., 1997; Panayotova M., Velikov B., 2003; Alvarez-Ayuso E. et al., 2003).

Before observing the variation shown by the three different metals in the investigated samples, it is important to notice some chemical-physical characteristics that can determine important influences in the selectivity and adsorption of samples towards these elements. First of all, the pH of the water solution is a remarkable parameter that regulates the adsorption processes (Elliott H.A., Huang C.P., 1981), when typically an increase in metals removal corresponds to increasing values of pH (Huang C.P., Ostovic F.B., 1978). Besides, pH is able to influence the speciation of different metals (Lin C.Y., Yang D.H., 2002). Other parameters of fundamental interest are the content of humic substances and clay; these elements are often able to immobilize and to hold back a high number of metals and other elements. Relatively to the selectivity of the used zeolite with respect to lead, copper and zinc, it is possible to observe the following trend: ZCL-ZNY $_{\text{purified wastewater}}$ Pb ≈ Cu ≈ Zn; ZCL-ZNY $_{\text{polluted wastewater}}$ Pb > Cu.≈ Zn. Also in this case the observed sequence results completely different in comparison to some researches, while it confirm the results of other studies (Hui K.S. et al., 2005). Also in this case, as observed before, the selectivity to elevated concentrations results the same for Clinoptilolite and the yellow Neapolitan tuff.

Examining the different elements, it is possible to observe that samples show completely dissimilar behaviours with respect to lead adsorption at low and high concentrations. In the case of purified wastewater, in almost all the samples, with few exceptions, a release of such metal is observed, however never at toxic levels. When a wastewater strongly polluted has been used, in all the samples, especially in those containing the most elevated percentages of zeolite, it is often possible to observe an elevated demolition power with removal efficiencies near to 100%. These behaviour results of fundamental importance indeed clearly show that the utilised samples behave, at low concentrations, as lead donors, while at higher concentrations they work as real demolition systems. Besides, similar behaviour shows remarkable performance aptitudes of the two zeolites despite the pH conditions were particularly unfavourable: basic to low concentrations (condition that favor the adsorption), and acid to high concentrations (condition that favor the release). Also, copper shows different behaviours in function of its concentration. As for lead, in the treatments with purified wastewater, under conditions of neutral or slightly alkaline pH, the samples bring copper in solution without ever reaching toxic levels. In the following treatments with the polluted wastewater, the samples show remarkable removal efficiencies both in those with only a pedological matrix, and with mixtures soil-zeolite that with only mineral matrix.

Zinc also shows different behaviours at low and high concentrations. In fact, in treatments with purified wastewater the samples bring zinc into solution, while in treatments with polluted wastewater both the samples with only soil, with mixtures soil-zeolite and with only zeolite show remarkable removal efficiencies.

Observing all the samples, a behaviour remarkably suitable for their use in the environmental sector is evident. In fact, in the case of purified wastewater, the mixtures soil / zeolite slowly release the different elements investigated that, with the exception of lead, to low observed concentrations, as noticed in previous researches, work as fertilizers, (Colella C., 2002; ZEOCEM, 2004; Reha'kova' M. et al., 2003; McGilloway R.L. et al., 2003; Sopkova' To et al., 1990). At high concentrations, such as those found in polluted wastewater, all the investigated samples, with particular reference to those containing the greatest percentages of zeolite, show elevated removal efficiencies despite a particularly acid environment unfavourable to the adsorption mechanisms. For such reasons the research has shown that the use of such samples, in relationship to the investigated elements, could constitute a main point in the environmental protection sector and particularly in soil remediation, in wastewaters purification, in the wastewater exploitation in several sectors, in agriculture (as fertilizer), etc. Besides, the adsorption aptitudes contribute to prevent possible groundwater pollution .

Table 1 Removal efficiency of Pb, Cu and Zn by zeolite/soil models

Parameter		Soil		Zeolite		Soil +Zeolite	
		+ efficiency	– efficiency	+ efficiency	– efficiency	+ efficiency	– efficiency
Pb	purified wastewater	SOT	SCV	ZNY	ZCL	ZCL-SCV (50%-50%) ZCL-SCV (25%-75%) ZCL-SOT (25%-75%)	ZNY-SCV (50%-50%)
Pb	polluted wastewater	SOT	SCV	ZCL	ZNY	ZNY-SCV (50%-50%) ZNY-SOT (50%-50%) ZCL-SCV (50%-50%) ZCL-SOT (25%-75%)	ZNY-SCV (25%-75%)
Cu	purified wastewater	SOT	SCV	ZCL	ZNY	ZCL-SCV (50%-50%)	ZNY-SCV (25%-75%)
Cu	polluted wastewater	SOT	SCV	ZNY	ZCL	ZCL-SOT (50%-50%)	ZCL-SCV (25%-75%)
Zn	purified wastewater	SOT	SCV	ZCL	ZNY	ZCL-SCV (50%-50%) ZCL-SCV (50%-50%)	ZNY-SCV (50%-50%)
Zn	polluted wastewater	SOT	SCV	ZNY	ZCL	ZCL-SCV (50%-50%)	ZCL-SOT (25%-75%)
SOT: Soil of Ottana; SCV: Soil of Castel Volturno; ZNY: Yellow Neapolitan Tuff ; ZCL: clinoptilolite							

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